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Analytical solution to a growth problem with two moving boundaries

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Abstract

The equation of motion for two moving reaction boundaries in a solid is analysed. The distance between the two boundaries corresponds to a film, and its thickness is given by an analytical expression in terms of the Lambert W function. The time dependent growth of the film thickness is discussed, including its limits.
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1. Introduction

The relationship between the conversion of a solid reactant with a fluid and the reaction time is of great importance in chemical reaction engineering. The *unreacted core shrinking model* and the *progressive conversion model* are the most fundamental models and favoured because of their analytical solutions [1,2].

We present a model for the evolution of a film thickness during reaction [6], which takes into account not only a moving boundary for the unreacted core, but also a changing size of the object itself, which is a second moving boundary. The motion of the former boundary is governed by a

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diffusion process and yields a squareroot-like behavior. The motion of the latter boundary is governed by chemical reaction and causes a linear decrease of the sample thickness.

This model is more advanced than the two basic ones mentioned above, but it can be solved analytically, provided that the Lambert W function (furtheron noted W) is applied. The W function [3,4] frequently applies to the study of biological growth problems in population dynamics [5] and, more recently, to film growth phenomena [6,7].

For flat objects, an exact and explicit solution for the film thickness is found. This model originated from the need to predict the film thickness in activated carbon as a function of reaction time, material properties, and process parameters.

Its justification is given by experimental observations made during the activation of glassy carbon [8]. Its significance is given by the fact that electrodes made from such activated carbon are utilized in electrochemical capacitors with the highest power density reported so far [9].

Thanks to the universal nature of the problem, the solution provided here is applicable to any system which is governed by its underlying differential equation. Specific potential applications of the model include the oxidation/reduction of metal catalysts, and the swelling of gels and coals.

2. Description of the model

A reaction \mathcal{R}_b creates a film on a particle according to the unreacted core shrinking model and is controlled by the diffusion from the surface of the planar slab to the reaction front and sustaining the progress of reaction [1,2]. Another process \mathcal{R}_a burns off the film at the outer sample boundary and is controlled by the chemical reaction.

\mathcal{R}_a and \mathcal{R}_b are two competing processes. Process \mathcal{R}_a leads to a shrinking of the whole particle itself and is retarding the film growth of reaction \mathcal{R}_b . The film thickness D as a function of reaction time therefore depends on both processes.

Note that in the standard treatment [1,2] of the shrinking unreacted core, the overall sample diameter is considered constant, whereas our model also accounts for the shrinking (or swelling) of the overall sample size. We refer to the *particle* as the unreacted core surrounded by the reacted film.

We assume that the reaction front of \mathcal{R}_a is confined to the particle surface and reaction \mathcal{R}_b confined to the unreacted core surface.

Consider a slab with thickness L in the halfspace $x \geq 0$ (Fig. 1).

Reaction \mathcal{R}_b takes place at $x = L$ with the result that the slab experiences structural changes—a film with a structure (like active carbon, open for diffusion of fluids) different from the original slab structure (carbon with closed pores, not open for diffusion of fluids) is growing either into the interior of the slab or growing on the surface of the slab. This reaction is confined to a plane front parallel to the outer slab surface. An example for swelling samples would be the growth of an oxide layer on a shrinking metal particle.

Reaction \mathcal{R}_b depends on the reaction partners coming by diffusion from the slab surface to the reaction front and maintaining the reaction. Let the position of the reaction front at time t' is Q .

Another reaction \mathcal{R}_a occurs with the result that the slab changes its original thickness P either by growing or by shrinking. This reaction is confined to the outer surface of the slab. The position

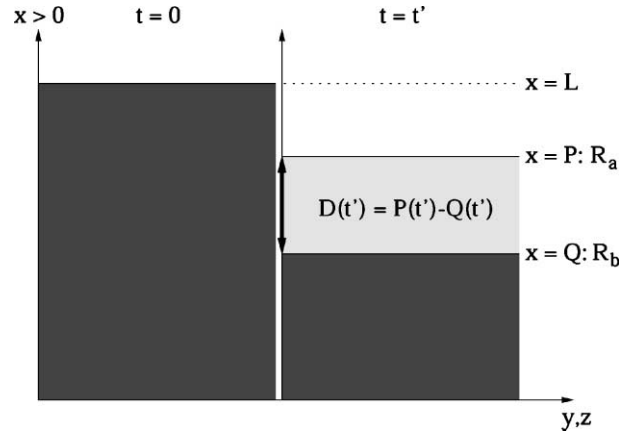


Fig. 1. Sketch displaying thickness changes during reactions \mathcal{R}_a and \mathcal{R}_b .

of the surface of the slab at time t' is P . At the same time the film thickness is $D(t')$, and the unreacted core thickness is $Q(t')$.

The initial condition is $D(t=0) = 0$. The change of the sample thickness (i.e., the burn-off) is assumed to be linear in t :

$$P(t) = L - at, \quad (1)$$

a being a constant characterizing reaction \mathcal{R}_a . Depending on the sign of a , $\dot{P} = -a$ may be positive or negative. For $a \geq 0$, the slab is burnt off after $t'' = L/a$. The function of $Q(t)$ is unknown.

We are interested in the thickness of the film with the open structure:

$$D(t) = P(t) - Q(t). \quad (2)$$

The change of $D(t)$ during reaction \mathcal{R}_b is directly linked to the change of $Q(t)$. The transport of reaction partners through the film is limited by the thickness D with the result that \dot{Q} is reciprocal to D :

$$\dot{Q}(t) = \frac{-b}{P(t) - Q(t)} = \frac{-b}{D(t)}, \quad (3)$$

b being a diffusion constant for reaction \mathcal{R}_b . The complete derivation of Eq. (3) is exercised elsewhere [6].

The model is based on the well established steady-state approximation, that the shrinking of the un-reacted core is much slower than the diffusion of the reactants. Using the time derivative of Eq. (2), we obtain an ordinary differential equation for $D(t)$:

$$\dot{D}(t) = -a + \frac{b}{D(t)}. \quad (4)$$

In the present section, we will apply variable transformations and a simple integration to obtain an implicit equation for $D(t)$. Using the W function, the analytical integral of Eq. (4) is obtained.

3. Solution and discussion of the differential equation

By bringing Eq. (4) into dimensionless form and splitting a constant off, we can integrate by variable separation and obtain

$$W(t^*) \exp(W(t^*)) = t^*, \quad (5)$$

which is the implicit representation of the W function [3,4].

The film thickness $D(t)$ is obtained by returning to the original variables:

$$D(t) = \frac{b}{a} \left(1 + W \left(- \exp \left(-1 - \frac{a^2}{b} t \right) \right) \right). \quad (6)$$

This solution is similar to the *generalized Lambert W function* G [5].

Although Eq. (4) can be solved numerically, it is advantageous to formulate it in the W -form, because the whole theory of the W -function becomes available. This facilitates the understanding of the solution and the implementation of the film thickness in more complex relations.

In addition, there exists already a fast and reliable algorithm to compute the W -function (Briggs, [7]).

Some typical results which reflect actual data obtained from glassy carbon activation [8], are displayed in Fig. 2. It is obvious that $D(t)$ increases with increasing diffusion constants, as expected from the model.

3.1. Limits of $D(t)$ for long time and slow film growth

The property of W ,

$$W(-\exp(-1)) = -1 \quad (7)$$

ensures that $D(t = 0) = 0$. On the other hand, using $W(0) = 0$ we find the limit of $D(t)$ for long reaction times t ,

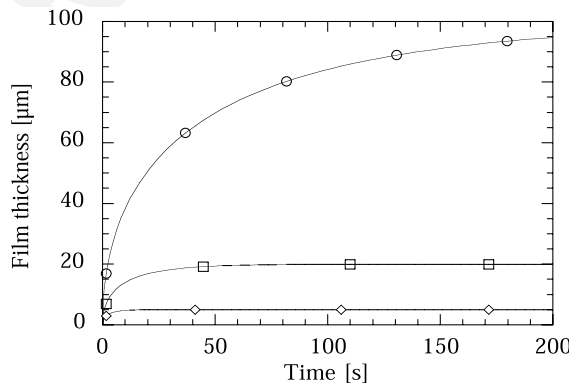


Fig. 2. $D(t)$ for three realistic sets of parameters a , b : $b = 0.1 \mu\text{m}^2/\text{s}$, circles; $b = 0.02 \mu\text{m}^2/\text{s}$, squares; $b = 0.005 \mu\text{m}^2/\text{s}$, diamonds; $a = 0.001 \mu\text{m}/\text{s}$.

$$\lim_{t \rightarrow \infty} D(t) = \frac{b}{a}, \quad (8)$$

provided that the slab has a sufficient thickness and is not yet burnt off.

The constant steady-state film thickness is approached asymptotically by an exponential of the form $\exp(-t_1)$, as can be derived from the argument in W .

As implied in the definition of t_1 , Eq. (5), the *time constant* characterizing the approach towards steady-state thickness is given by $\tau = b/a^2$. This time decreases if the diffusion constant b is decreased, or if the burn-off rate a is increased, with the latter one being dominant because of its second power ('burn-off wins').

With the film growth rate b taken zero, no film at all is obtained. This can be drawn from the steady-state film thickness, Eq. (15), but also from the corresponding limit of W ,

$$\lim_{b \rightarrow 0} D(t) = \lim_{b \rightarrow 0} \frac{b}{a} \left(1 + W \left(- \exp \left(-1 - \frac{a^2}{b} t \right) \right) \right) = 0. \quad (9)$$

3.2. Limiting behavior for slow burn-off

With the burn-off rate a taken zero, the diffusion limited film thickness with non-changing sample thickness must be obtained. To verify this point, we use the series expansion [5] of the generalized Lambert W function G [5], which up to fourth order is given by

$$G(t_1) = \sqrt{2}\sqrt{t_1} - \frac{2}{3}t_1 + \frac{\sqrt{2}}{18}t_1^{3/2} + \frac{2}{135}t_1^2. \quad (10)$$

The explicit result for the film thickness for small values of a is thus given by

$$D(t) = \sqrt{2bt} - \frac{2}{3}at. \quad (11)$$

For $a = 0$, only the lowest order term remains, and therefore

$$\lim_{a \rightarrow 0} D(t) = \sqrt{2bt}, \quad (12)$$

as expected for diffusion controlled film growth on non-shrinking flat samples [1,2].

A plot of this lowest order approximation is shown as the upper, dashed curve in Fig. 3. It corresponds to the classical diffusion controlled film growth for a non-shrinking sample. The solid line represents the complete solution, Eq. (13).

Also, the first order approximation (Eq. (18)) does not reflect the correct film growth, as shown in the lowest dashed curve in Fig. 3. Moreover, this approximation leads to a maximum of the film thickness (at time $t = 9/8\tau$), which is not justified by the model.

The comparison shows that the influence of non-zero burn-off is very significant for large times, and is responsible for the approach towards a steady-state thickness. Omission of the burn-off would lead to completely erroneous estimates of the film thickness for longer times.

Knowledge of Lambert's W function has been essential for deriving an analytical solution that correctly describes the time-dependent film thickness for both short and long time scales.

We finally note that the reaction controlled growth (concentration of reactants in the film does not change) is governed by equation

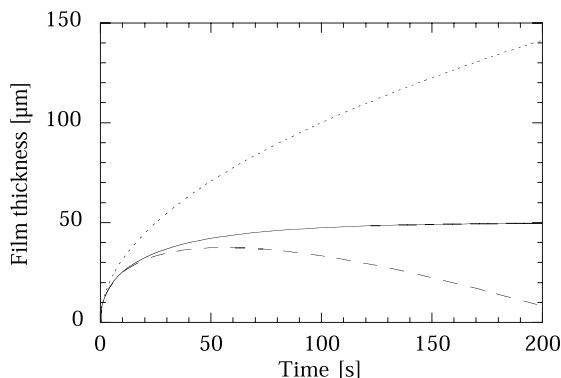


Fig. 3. $D(t)$ for $a = 0.001 \mu\text{m/s}$ and $b = 0.05 \mu\text{m}^2/\text{s}$ from Eq. (13) (solid line) and from the lowest (upper curve, Eq. (19)) and first (lower curve, Eq. (18)) order approximation.

$$\dot{Q}(t) = \frac{b^*}{a} \dot{P}(t), \quad (13)$$

b^* being a constant describing the reaction rate, and $D(t)$ being a linear function of the reaction time:

$$D(t) = (b^* - a)t. \quad (14)$$

Such a growth is actually observed in electrochemically activated carbon [10].

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